

## NO DRAWINGS

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## (54) A METHOD OF MAKING A DOPED SEMI-CONDUCTOR MATERIAL

(71) We, CESKOSLOVENSKA AKADEMIE VED, a Czechoslovakian Corporation, of No. 3 Narodni, Praha 1, Czechoslovakia, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of making doped semi-conductor material having p-type conductivity.

Heretofore the actual practice of making doped semi-conductor crystals and layers with satisfactory accuracy was still a process technically very difficult to perform, especially for crystals or layers with p-type conductivity. The concentration of doping agent desired in the crystal or in the epitaxial layers was achieved by admixing a gaseous doping substance with a carrier gas or with gas constituting a protective atmosphere wherein a crystal or layer is grown. The amount of the doping agent added to the gas is always very small, varying in most cases between hundredths down to units of p.p.m. Such a low concentration of the doping agent can be continuously metered only with great difficulty and by means of very complicated apparatus. Many producers of semi-conductors employ a mass spectrograph in order to control the composition of the gaseous mixture. Therefore, only such methods must be adopted for preparing gaseous mixtures which can assure a precise composition for the mixture either as a stream or as a protective atmosphere.

Usually, in the production of semi-conductors of p-type conductivity a multiple diluted mixture of hydrogen with a small amount of gaseous diborane  $B_2H_6$  as doping agent from a pressure flask if used. Practical experience has shown that this doping method is in no way precise. For instance, the producers of plants for epitaxial growth guarantee that the said doping method has a lower accuracy for conductivity of the p-type than for conductivity of the N-type. One source of this lower

accuracy lies in the fact that the mixture obtained with the doping agent from the pressure flask must then be diluted in a ratio of approximately 1:100. Because the diluting gas is never absolutely pure, as it always contains moisture and oxygen, the doping agent can react with impurities after the formation of the mixture. Thereby, the amount of doping agent in admixture with the carrier gas is subject to substantial variation.

It has previously been proposed to make doped semi-conductor material by a method comprising depositing semi-conductor material from a mixture of a gaseous compound of the semi-conductor material, a vapour from a solid doping agent and a carrier gas, on a heated carrier body of the same semi-conductor material in a reaction chamber; to use in said method solid doping agents exhibiting a wide range of vapour pressures over a convenient temperature range; and, in forming the mixture of said method, to pass a stream of carrier gas over the solid doping agent which by way of illustration may be decaborane ( $B_{10}H_{14}$ ) when p-type semi-conductor materials are desired.

According to the present invention, we provide a method of making doped semi-conductor material having p-type conductivity, comprising forming a gaseous mixture containing a carrier gas, semi-conductor forming material and a vapour of one or more of the following substances as doping agent: boranes of the formulae  $B_{10}H_{14}$ ,  $iB_{11}H_{18}$ ,  $B_{10}H_{16}$ , and  $B_{10}H_{20}$ , the halogen derivatives of said boranes, and the halogen derivatives of decaborane, and depositing semi-conductor material from the mixture.

Preferably, the formation of the gaseous mixture includes creating a gaseous flow of a mixture of carrier gas and semi-conductor forming material past the outlet end of a capillary tube communicating at its inlet end with a source of the vapour so as to extract the vapour from the capillary tube into the gaseous flow and thereby mix the vapour with the gaseous flow.

By virtue of the present invention it is possible to produce precisely epitaxial layers and crystals of semi-conductors having any required specific resistance; that is, for each desired specific resistance a doping agent of suitable vapour pressure is available which enables the preparation of a corresponding mixture without the need for any auxiliary dilution.

As doping agents suitable halogen derivatives include fluoro-, chloro-, bromo- and iodo-tridecahydrodecaboranes. The general preparations and isolation and some properties of the said boranes are described in Collection of Czechoslovak Chemical Communications: Vol. 31 (1966) 4744, Vol. 32 (1967) 1095 and especially Vol. 33 (1968) 699 dealing with a novel stable borane  $B_{10}H_{12}$ .

By selecting a capillary tube of suitable diameter and length the amount of doping agent in the mixture can be controlled. Also, selection of the borane is made according to the volatility of the same, the latter being always inversely proportional to its molecular weight. This rule is applicable also to the halogen derivatives of the boranes. In such a manner it is possible to select always the most suitable doping agent for any desired specific resistance of the semi-conductors.

#### EXAMPLE 1

Through a capillary tube of a diameter 3 mm and length 100 mm the doping vapour is introduced from a container for the doping agent into a main pipe-line through which a gaseous mixture of carrier gas e.g. hydrogen and 1%  $SiCl_4$  flows at a velocity of 50 litres per minute to a doping box. The flow is past the outlet of the capillary tube and serves to extract the doping vapour from the capillary tube and serves to extract the doping vapour from the capillary tube so that the vapour intermixes by diffusion with the gaseous flow. The resulting mixture enters the doping box where a monocrystalline silicon is heated to a temperature of 1273° K, whereby the growing of an epitaxial layer takes place, this layer having a specific resistance 1 ohm/cm and a thickness which depends on the time of exposure of the surface area of the heated monocrystalline silicon. In such a manner for instance transistors or other elements are produced.

The length of the capillary tube and the temperature used govern the resultant resistance of the epitaxial layer as determined by the equation

$$N = D \frac{A}{LRT} (p - p_0)$$

wherein

N is the amount of moles of doping agent introduced into the gas stream to produce the mixture which induces the growth of an epitaxial layer in unit time,  
D is the diffusion coefficient of the doping agent at the selected temperature of the capillary tube,  
A is the cross section of the capillary tube,  
L is the length of the capillary tube,  
p is the pressure of the doping agent in its container,  
p<sub>0</sub> is the pressure of the doping agent in the streaming gas mixture,  
R is a gas constant,  
T is the absolute temperature in the container for the doping agent.

#### EXAMPLE 2

The following is tabulated data for using octadecaborane of the formula  $B_{18}H_{22}$  in admixture with hydrogen as the carrier gas in order to produce an epitaxial layer having any desired or required specific resistance:

An amount of hydrogen saturated with octadecaborane	Resistance:
200 ml/min	8.5 ohm/cm
300 ml/min	5.9 ohm/cm
400 ml/min	4.9 ohm/cm
600 ml/min	3.8 ohm/cm
1000 ml/min	2.8 ohm/cm

#### WHAT WE CLAIM IS:—

1. A method of making doped semi-conductor material having p-type conductivity, comprising forming a gaseous mixture containing a carrier gas, semi-conductor forming material and a vapour of one or more of the following substances as doping agent: boranes of the formulae  $B_{18}H_{22}$ ,  $iB_{18}H_{22}$ ,  $B_{20}H_{16}$  and  $B_{10}H_{12}$ , the halogen derivatives of said boranes, and the halogen derivatives of decaborane, and depositing semi-conductor material from the mixture.

2. A method according to Claim 1, wherein the formation of the gaseous mixture includes creating a gaseous flow of a mixture of carrier gas and semi-conductor forming material past the outlet end of a capillary tube communicating at its inlet end with a source of the vapour so as to extract the vapour from the capillary tube into the gaseous flow

and thereby mix the vapour with the gaseous flow.

3. A method of making doped semi-conductor material, according to either of the Ex-  
5 amples.

4. A doped semi-conductor material whenever obtained by the method of any one of the preceding claims.

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